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Thermodynamic States in Explosion Fields

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Abstract. We investigate the thermodynamic states occurring in explosion fields from condensed explosive charges. These states are often modeled with a Jones-Wilkins-Lee (JWL) function. However, the JWL function is not a Fundamental Equation of Thermodynamics, and therefore cannot give a complete specification of such states. We use the Cheetah code of Fried to study the loci of states of the expanded detonation products gases from C-4 charges, and their combustion products air. In the *Le Chatelier Plane* of specific- internal-energy versus temperature, these loci are fit with a *Quadratic Model* function $u(T)$, which has been shown to be valid for $T < 3,000$ K and $p < 1$ k-bar. This model is used to derive a Fundamental Equation $u(v,s)$ for C-4. Given $u(v,s)$, one can use Maxwell's Relations to derive all other thermodynamic functions, such as temperature: $T(v,s)$, pressure: $p(v,s)$, enthalpy: $h(v,s)$, Gibbs free energy: $g(v,s)$ and Helmholtz free energy: $f(v,s)$; these loci are displayed in figures for C-4. Such complete equations of state are needed for numerical simulations of blast waves from explosive charges, and their reflections from surfaces.

Introduction

Here we investigate the thermodynamic states occurring in explosion fields from the detonation of condensed explosives in air. In typical applications, the pressure of expanded detonation products gases is modeled by a Jones¹-Wilkins²-Lee³ (JWL) function: $p_{JWL} = f(v, s_{CJ})$; constants in that function are fit to cylinder test data. This function provides a specification of pressure as a function of specific volume, v , along the expansion isentrope ($s = \text{constant} = s_{CJ}$) starting at the Chapman-Jouguet (CJ) state. However, the JWL function is not a fundamental equation^{4,5} of thermodynamics, and therefore gives an incomplete specification of states. For example, explosions inherently involve shock reflections from surfaces; this changes the entropy of the products, and in such situations the JWL function

provides no information on the products states. In addition, most explosives are not oxygen balanced, so if hot detonation products mix with air, they after-burn, releasing the heat of reaction via a turbulent combustion process. This raises the temperature of explosion products cloud to the adiabatic flame temperature ($\sim 3,000$ K). Again, the JWL function provides no information on the combustion products states.

This conundrum may be overcome by using the Cheetah code⁶ as an equation-of-state module. As inputs, one specifies the chemical composition of the substance and two thermodynamic variables; Cheetah then finds the thermodynamic equilibrium (or constrained equilibrium) solution by minimizing the Gibbs free energy of the system; the output is all thermodynamic variables at that state. This approach was used to analyze the thermodynamic states from the detonation of a C-4

charge ($\rho_0 = 1.6 \text{ g/cc}$) and the combustion of the detonation products with air.

History of the JWL Function

The Jones-Wilkins-Lee (JWL) function is an empirical Equation of State (EOS) used to describe the pressure of expanding detonation products gases. It is based on a function proposed first by Jones and Miller¹ in 1948:

$$p^J(V, T) = Ae^{-R \cdot V} - B + C \cdot T \quad (1)$$

where V denotes the volume ratio $V = v/v_0$ and T is temperature. And a function suggested by Mark Wilkins⁵ in 1964:

$$p^W(V, E) = \frac{\alpha}{V^Q} + B \left(1 - \frac{\omega}{RV} \right) e^{-R \cdot V} + \frac{\omega E}{V} \quad (2a)$$

along with its corresponding isentrope:

$$p_s^W(V) = \frac{a}{V^Q} + Be^{-R \cdot V} + \frac{C}{V^{\omega+1}} \quad (2b)$$

where $\alpha = a(Q-1)/(Q-1-\omega)$. These functions were extended to the following form by Ed Lee⁶ in 1968:

$$p^{JWL}(V, E) = A \left(1 - \frac{\omega}{R_1 \cdot V} \right) e^{-R_1 \cdot V} + B \left(1 - \frac{\omega}{R_2 \cdot V} \right) e^{-R_2 \cdot V} + \frac{\omega E}{V} \quad (3a)$$

along with its corresponding isentrope:

$$p_s^{JWL}(V) = Ae^{-R_1 \cdot V} + Be^{-R_2 \cdot V} + \frac{C}{V^{\omega+1}} \quad (3b)$$

Lee and co-workers established the *JWL* parameters (A, B, C, R_1, R_2 and ω) for a number of explosives by fitting the function to experimental *C-J* conditions, calorimetric data, and cylinder expansion data^{3,7,8,9}.

Lee and Tarver¹⁰ have developed an ignition and growth model for numerical simulations of shock initiation of heterogeneous explosives; it is based on the *JWL* function (3) and single pressure-dependent reaction rate equation. Clark Souers has

added additional rate equations to model more complex problems, such as detonation corner turning^{11,12,13}; often times this extension is called the *JWL++* model. The latest version of Souers multi-reaction-rate model is now called *Tarantula/JWL++*¹⁴. Recently, Carpenter¹⁵ and Tarver¹⁶ have questioned the adequacy of *JWL++* models to correctly simulate the energy release mechanism in non-ideal explosives. Here we assess the adequacy of the *JWL* representation of reactive flow modeling from a Thermodynamic perspective. To assist in this, Fundamental Equations of Thermodynamics are derived in Appendix A.

Pressure-Volume Plane

Figure 1 depicts the locus of states of the C-4 detonation products in the pressure-specific volume plane. The locus starts at the *Chapman-Jouguet (CJ)* state, and expands down the isentrope ($s_{CJ} = 1.768 \text{ cal/g-K}$) to atmospheric pressure. The locus was fit with the following *JWL* function:

$$p_{PG}^{JWL}(v, T) = A \left(1 - \frac{\omega \cdot v_0}{R_1 \cdot v} \right) e^{-R_1 \cdot v/v_0} + B \left(1 - \frac{\omega \cdot v_0}{R_2 \cdot v} \right) e^{-R_2 \cdot v/v_0} + R_{DP} T / v \quad (4)$$

where $A = 5.23 \text{ Mbar}$, $B = 0.154 \text{ Mbar}$, $R_1 = 4.30$, $R_2 = 1.70$ and $R_{DP} = 3.12 \text{ (bar-cc/g-K)}$. Note that for specific volumes larger than $\sim 10 \text{ cc/g}$, the function reduces to the perfect gas law.

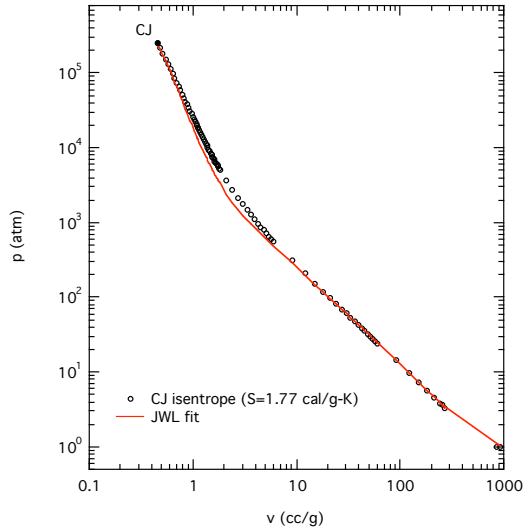


Fig. 1. Pressure-volume diagram depicts the locus of states of the detonation products gases as they expand down the CJ isentrope for a C4 charge. Locus is fit with the JWLV function (4).

Le Chatelier Plane

Figure 2 presents the same locus in the specific internal energy—temperature plane. Points (red circles) were calculated by the Cheetah code, assuming that the composition of detonation products was frozen¹⁷ for $T < 1,800$ K. The solution starts at the CJ point ($T_{CJ} = 3,238$ K) and expands down the isentrope ($s_{CJ} = 1.768$ cal/g-K) to room temperature. The standard energy of C-4 Reactants and Products at *stp* (1 atm, 298K) are: $u_{F,R}^0 = 73.114$ and $u_{F,P}^0 = -1,173.68$ cal/g, respectively; their difference is the heat of detonation: $u_{F,P}^0 - u_{F,R}^0 \equiv \Delta H_d = -1,248$ cal/g, and is indicated on the figure. Also shown in that figure is the *equilibrium* isentrope (blue curve), which assumes chemical equilibrium at all temperatures. At room temperature, it results in energy of -1,350 cal/g which disagrees with the measured heat of detonation. This effect is typical of condensed explosives; quenching induced by the strong rarefaction created when the DP gases expand from the CJ state stops the kinetic reactions¹⁷ at $\sim 1,800$ K. A Constant-Volume Detonation (CVD)

is represented by the $u = u_{F,R}^0$ line from R to P. It gives a CVD detonation temperature of 2,887 K.

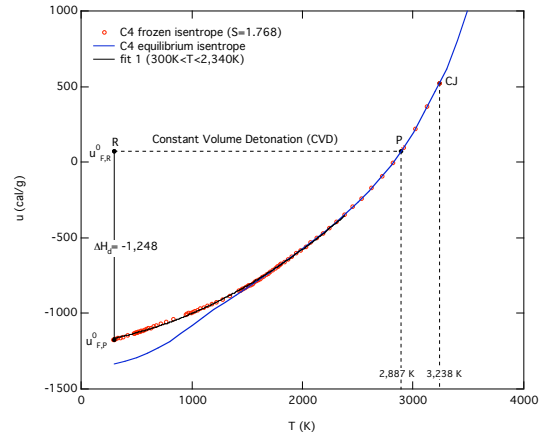


Fig. 2. *Le Chatelier* diagram depicting the locus of states of the detonation products of the explosive C-4, starting at the *Chapman-Jouguet* point (CJ) and expanding at constant entropy to one atmosphere.

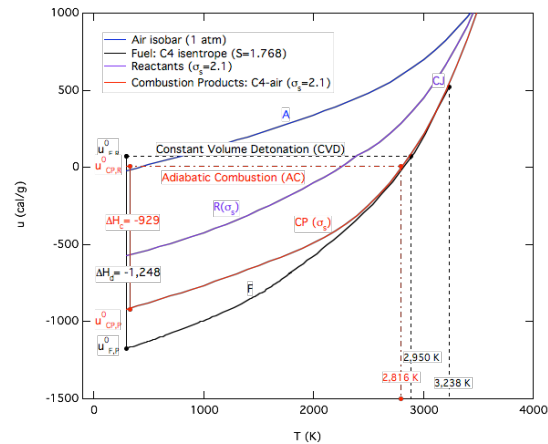


Fig. 3. *Le Chatelier* diagram depicting the locus of states for the detonation of a C-4 charge (curve F) and its stoichiometric combustion with air (curve CP). Also shown are loci of the reactants (curve R) and air (curve A).

Fig. 3 depicts the locus of states for the equilibrium products CP for the stoichiometric combustion of C-4 in air ($\sigma_s = 2.1$). The red line represents isobaric ($p = 1$ atm) combustion locus. The standard energy of C4-air Reactants and

Products at *stp* are: $u_{CP,R}^0 = +9.677 \text{ cal/g}$ and $u_{CP,P}^0 = -1,016.77 \text{ cal/g}$, respectively; their difference is the heat of combustion: $u_{CP,P}^0 - u_{CP,R}^0 = \Delta H_c = -929.04 \text{ cal/g}_m = -2,880 \text{ cal/g}_{C4}$, which is indicated on the figure. Adiabatic Combustion (AC) is represented by the $u = u_{CP,R}^0$ line from *R* to *P*. It gives an adiabatic combustion temperature of 2,816 K. For temperatures below 3,000 K, these curves are only a function of temperature.

Quadratic Model

Therefore the loci of states in Fig. 3 were fit with quadratic functions of temperature¹⁸:

$$u_k(T) = a_k T^2 + b_k T + c_k \quad (5)$$

for $k=F, A, R, CP$. The fitting constants: a_k, b_k, c_k are listed in Appendix B. This function then serves as caloric EOS for the detonation products and their combustion products with air.

In hydro codes, one typically carries the density ($\rho_k = 1/v_k$) and specific internal energy (u_k) as independent variables. For pure cells, given u_k , the above relation may be inverted to determine the temperature:

$$T_k = [-b_k + \sqrt{b_k^2 - 4a_k(c_k - u_k)}] / 2a_k \quad (6)$$

Then pressure is calculated from the perfect gas relation:

$$p = RT / v \quad (7)$$

We have shown¹⁸ that the above relation is valid for pressures less than one kilo-bar.

For computational cells containing a mixture of components, the mixture energy also satisfies a quadratic form:

$$u_m(T) = \sum_c Y_c u_c = a_m T^2 + b_m T + c_m \quad (8)$$

where the mixture coefficients are defined by the mass-weighted sums:

$$a_m = \sum_c Y_c a_c \quad \& \quad b_m = \sum_c Y_c b_c \quad (9, 10)$$

$$c_m = \sum_c Y_c c_c \quad \& \quad R_m = \sum_c Y_c R_c \quad (11, 12)$$

Given the mixture specific internal energy, u_m , the mixture temperature can be evaluated by solving (8) for T_m yielding:

$$T_m = [-b_m + \sqrt{b_m^2 - 4a_m(c_m - u_m)}] / 2a_m \quad (13)$$

Fundamental Equation

The above relations were used to derive the *Fundamental Equation* for the detonation products and combustion products:

$$u(s, v) = aT_*^2 e^{2s/c_v} (v_*/v)^{2R/c_v} + bT_* e^{s/c_v} (v_*/v)^{R/c_v} + c \quad (14)$$

where T_* and v_* represent the temperature and specific volume in the reference state denoted by subscript *. This function is displayed in Fig. 4.

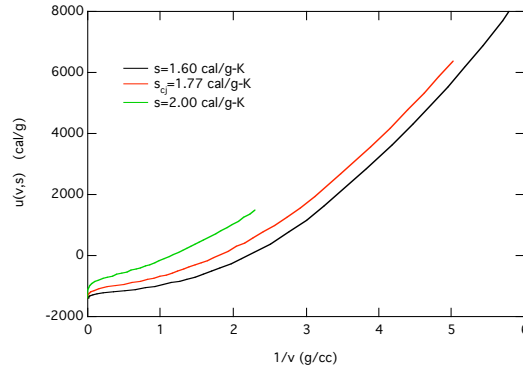


Fig. 4. The Fundamental Equation $u(v, s)$ for C-4 detonation products.

The specific internal energy for C4 detonation products is displayed as a function of temperature in Fig. 5. Below 2,200 K, the products behave as a perfect gas, and u is solely a function of temperature; at higher temperatures it is a function of both temperature and entropy.

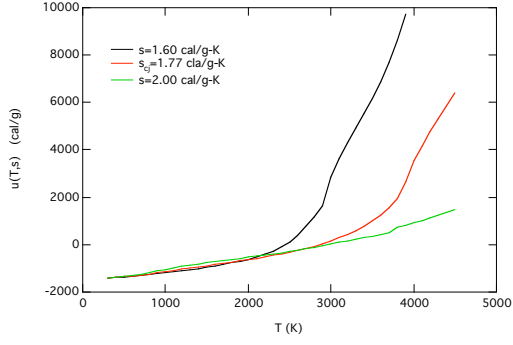


Fig. 5. Specific internal energy function $u(T,s)$ for C-4 detonation products.

Given an analytic form of fundamental equation: $u(s,v)$ one can use Maxwell's reciprocity relations^{4,5} to evaluate the corresponding temperature, T , pressure, p , and enthalpy, h , Gibbs free energy, g , and Helmholtz free energy, f :

$$T(s,v) \equiv \left(\frac{\partial u}{\partial s} \right)_v \quad (15)$$

$$p(s,v) \equiv - \left(\frac{\partial u}{\partial v} \right)_s \quad (16)$$

$$h(s,v) \equiv u(s,v) + p(s,v)v \quad (17)$$

$$g(v,s) = h(v,s) - Ts \quad (18)$$

$$f(v,s) = u(v,s) - Ts \quad (19)$$

These functions are displayed in Figs. 6-10 for C4 detonation products in terms of v and s .

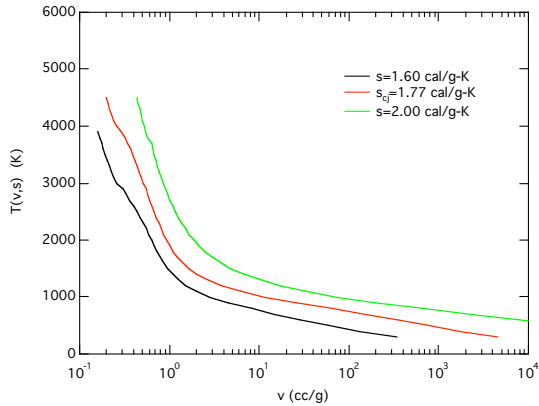


Figure 6. Temperature function $T(v,s)$ for C-4 detonation products.

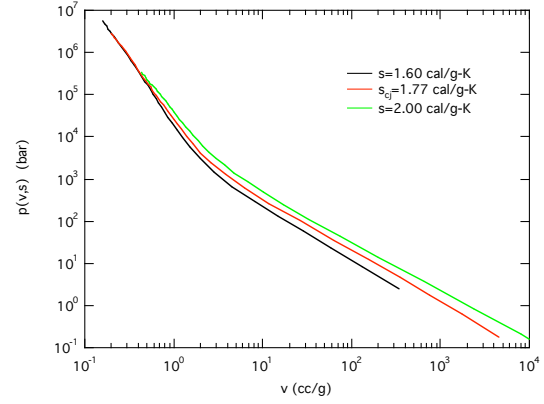


Figure 7. Pressure function $p(v,s)$ for C-4 detonation products.

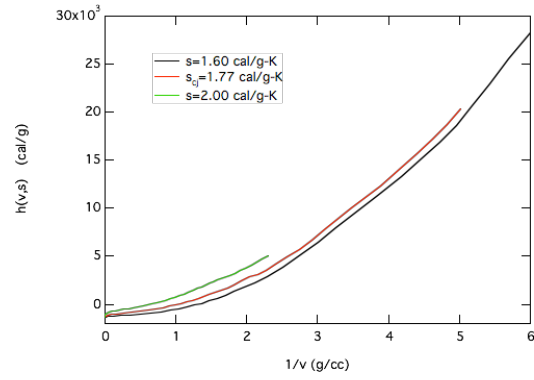


Figure 8. Specific enthalpy function $h(v,s)$ for C-4 detonation products.

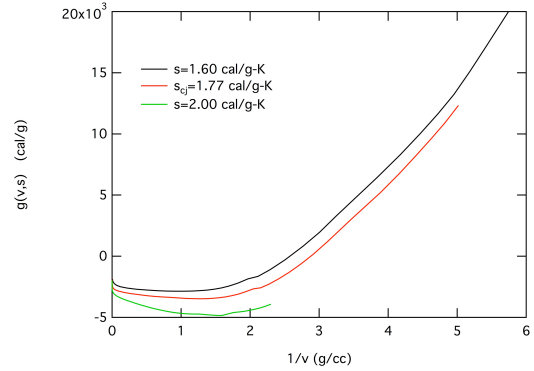


Figure 9. Specific Gibbs free energy function $g(v,s)$ for C4.

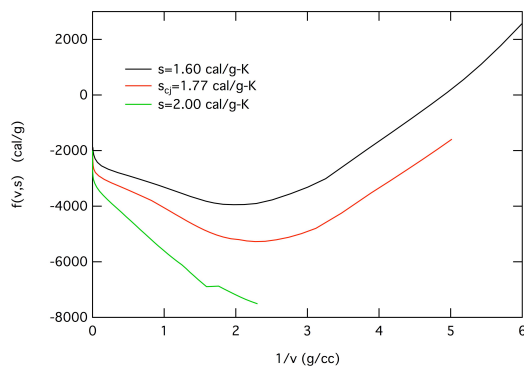


Figure 10. Specific Helmholtz free energy function $f(v,s)$ for C4 detonation products.

Conclusions

Blast waves from explosives charges typically involve reflections from nearby surfaces, which changes the entropy of the products. Also, mixing of the products with air leads to combustion, which raises the products cloud temperature to around 3,000 K. To capture these physical processes in numerical simulations, one needs a complete EOS. This can be provided by using the Cheetah code as an EOS subroutine, or by using the analytic specification of such loci by the Fundamental Equation presented here.

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Appendix A: Fundamental Equations

Here we describe the concept of fundamental equations in thermodynamics^a. We start with the First Law of thermodynamics for a pure single-phase substance:

$$1^{st} \text{ Law: } du = dQ^0 + dW^0 \quad (A1)$$

which says that the specific internal energy of a substance du may be changed by heat input: dQ^0 and work: $dW^0 = -pdv$. According to the first part of the Second Law of thermodynamics, the heat input may be expressed as $dQ^0 = Tds$ along a reversible path (denoted by superscript 0). Inserting these relations into (A1) yields:

$$1^{st} \text{ \& } 2^{nd} \text{ Laws: } du = Tds - pdv \quad (A2)$$

^a This exposition relies heavily on Chapter 12 of Joseph Kestin’s book: *A Course in Thermodynamics*⁴ and Herbert Callen’s book: *Thermodynamics*⁵.

Now du is a perfect differential (a *Pfaffian form*), so the above relation implies that u must be a function of specific entropy, s , and specific volume, v , that is

$$u = u(s, v) \quad (A3)$$

Its total differential may be expressed as:

$$du = \left(\frac{\partial u}{\partial s} \right)_v ds + \left(\frac{\partial u}{\partial v} \right)_s dv \quad (A4)$$

Assuming that the specific internal energy function $u(s, v)$ is both a C^3 (differentiable) function and obeys the First and Second Laws of thermodynamics, then comparison of (A2) and (A4) shows that there must be a relation between the derivatives of internal energy and the thermodynamic variables of temperature and pressure:

$$T(s, v) = \left(\frac{\partial u}{\partial s} \right)_v \quad (A5)$$

$$p(s, v) = - \left(\frac{\partial u}{\partial v} \right)_s \quad (A6)$$

These are known as *reciprocity relations*, first discovered by James Clerk Maxwell in 1864. Given $u = u(s, v)$, one could evaluate the temperature $T(s, v)$ from (A5) and pressure $p(s, v)$ from (A6), and then eliminate entropy between them to find the thermal equation of state:

$$F(p, v, T) = 0 \quad (A7)$$

One could also calculate the enthalpy of the substance and its specific heat:

$$h(s, v) = u(s, v) + p(s, v)v \quad (A8)$$

$$c_v(s, v) \equiv \left(\frac{\partial u}{\partial T} \right)_v = \left(\frac{\partial u}{\partial s} \right)_v \left(\frac{\partial T}{\partial s} \right)_v \quad (A9)$$

Thus, if the function $u = u(s, v)$ is known, one can calculate all thermodynamic variables of a system: p, T, h, c_v , etc. In recognition of this property, $u = u(s, v)$ is known a *fundamental equation* in thermodynamics; it is a function of its canonical variables s and v . For a perfect gas, it acquires the form:

$$u(s,v) = c_v T^* \left\{ \left(\frac{v^*}{v} \right)^{R/c_v} e^{s/c_v} - 1 \right\} \quad (A10)$$

which may be derived from the perfect gas relations:

$$u = c_v (T - T^*) \quad (A11)$$

$$s = c_v \ln \frac{T}{T^*} \left(\frac{v}{v^*} \right)^{R/c_v} \quad (A12)$$

by elimination of the temperature.

One can prove that there exist three additional fundamental equations, each utilizing its own particular canonical variables:

specific enthalpy:

$$h(p,s) = u(s,v) + p(s,v)v \quad (A13)$$

Helmholz free energy:

$$f(v,T) = u(s,v) - Ts \quad (A14)$$

Gibbs free energy:

$$g(p,T) = h(p,s) - Ts \quad (A15)$$

The Mollier diagram $h = h(p,s)$ is a graphical representation of a fundamental equation locus in thermodynamic space. Comparison of (1) with (A3) and (A13)-(A15) proves that the JWL function is not a fundamental equation, and therefore cannot give a complete specification of thermodynamic states.

Appendix B: Fitting Constants for the Quadratic Model

Table B1. Piecewise quadratic fits: $u_F = a_i T^2 + b_i T + c_i$ of the CJ isentrope of C-4 detonation products

REGION i	a_i	b_i	c_i
1: $300K < T < 2,340K$	11.309×10^{-5}	0.085576	-1,199.7
2: $2,340K < T < 3,700K$	82.435×10^{-5}	-3.6012	3,570.1
3: $3,700K < T < 4,150K$	182.47×10^{-5}	-7.787	5,328.8
4: $4,150K < T < 4,900K^*$	210.03×10^{-5}	-12.849	21,607

* u exists only for $T < 4,900K$

Table B2. Piecewise quadratic fits: $u_P = a_i T^2 + b_i T + c_i$ for isobaric combustion of C-4 detonation products in air ($\sigma_s = 2$)

REGION i	a_i	b_i	c_i
1: $300K < T < 2,340K$	4.6×10^{-5}	0.14816	-962.62
2: $2,340K < T < 3,700K$	62.137×10^{-5}	-2.4658	2,026.7
3: $3,700K < T < 4,150K$	-111.68×10^{-5}	9.9347	-20,080
4: $4,150K < T < 4,350$	-36.05×10^{-5}	3.7283	-7,345.4
5: $4,350K < T < 6,000K$	40.904×10^{-5}	-3.4458	9,386

$M_{CP} = 27.5$ at $T = 2,800 K$